Structural and Vibrational Study of Heme Carbonyls With Solid-State Interactions

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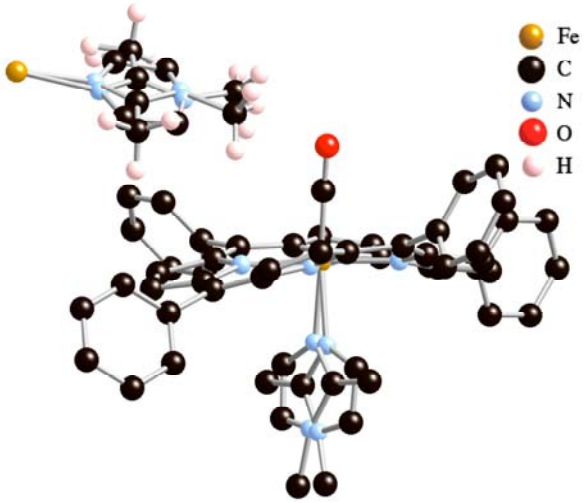
We report the molecular structures and spectroscopic data of four low-spin (carbonyl)iron(II) tetraphenylporphyrinates, [Fe(TPP)(CO)(L)], where L = 1-methylimidazole, 2-methylimidazole, 1,2-dimethylimidazole (no solvate) and 1,2-dimethylimidazole (toluene solvate). These four derivatives show a large range of CO stretching frequencies in the solid-state (1926-1968 cm^{-1}). This variation from the canonical 1970 cm^{-1} CO stretching frequency observed in carbonyl hemes results from solid-state interactions. Molecules of the [Fe(TPP)(1,2-Me_2Im)(CO)] and [Fe(TPP)(2-MeHIm)(CO)] toluene solvates pack into lattices that place the imidazole from an adjacent molecule near the carbonyl group. In [Fe(TPP)(2-MeHIm)(CO)] hydrogen interactions from an N–H imidizole shift the CO stretching frequency to 1926 cm^{-1}. The toluene solvate of [Fe(TPP)(1,2-Me_2Im)(CO)] has a disordered 1,2-dimethylimidazole (62%/38%) that creates two distinct environments for CO and result in the splitting of the CO stretching frequency. The high precision of these four structures allows us to make a number of structural and spectroscopic correlations that describe the Fe–C–O unit, and the nonbonding interactions in the solid-state. The interactions described are closely related to the large range of CO stretching frequencies, 1904 to 1984 cm^{-1}, observed in heme proteins and specific interactions observed in carbonmonoxy myoglobin.



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